Integration of nanofiltration and bipolar electrodialysis for valorization of seawater desalination brines: production of drinking and waste water treatment chemicals

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Abstract

Nanofiltration (NF), as a selective Mg(II) and Ca(II) separation and concentration treatment, and electrodialysis with bipolar membranes (EDBM) were evaluated for the valorization of seawater desalination reverse osmosis brines (60 gNaCl/L) to produce both rich Mg(II) and Ca(II) brines for phosphate recovery and HCl and NaOH as chemicals for desalination treatments.

A NF pilot plant, using NF270 membranes at 20 bars, provided a rich Mg(II) (8.3 gMg(II)/L) and Ca(II) (2.1 gCa(II)/L) brine on the concentrated stream with enrichment factors of 3.2 for Mg(II) and 2.5 for Ca(II). The NF permeate stream containing 50±2 gNaCl/L was treated to remove residual Mg(II) (760mg/L) and Ca(II) (415mg/L) by chemical precipitation with Na_2CO_3 and NaOH before the EDBM unit. Divalent cations free brine containing NaCl (50 gNaCl/L) were fed into the EDBM stack in order to produce NaOH and HCl under recirculation configuration. Constant voltage and acid and base concentrations at different initial conditions were evaluated to obtain the maximum acid and base concentration (approximately 1 M NaOH/HCl) at 9 V. No substantial effect of initial acid and base concentrations on the overall performance was observed. An energy consumption of 2.6 kWh/kgNaOH and current efficiency of 77±3 % were calculated.

Keywords: Divalent ions; Seawater brine; Chemical precipitation; Purification; Acid – base production

1. INTRODUCTION

Water stress increases due to population rise and the uncontrolled expansion of industrial and agricultural activities are critical issues in many regions all over the world [1]. For this reason, obtaining new water sources to supply the expected increasing demand, 100 million m^3/day by 2015 [2], has become an important research and development topic. Among the several possibilities, seawater desalination (SWD) has been identified as one of the preferred options to obtain fresh water and the number of desalination plants is continuously increasing. Reverse osmosis (RO) is the most used technology for SWD due to the significant improvements in new membranes development (new materials, lifetime lengthening, …) in addition to advances in energy recovery systems and also in the pre-treatment processes [3]. However, one of the drawbacks of this technology is the disposal of the produced brine, which accounts for the 50% volume of treated seawater with approximately doubled salt concentration. Usually, this brine is directly discharged back into the sea, generating environmental impacts in the reception point such as diminishing the amount of flora and creating salinity gradients and, most important, increasing the OPEX cost of desalination plants due to the energy consumption in pumping the brine [4,5]. For this reason new desalination projects promote the integration of RO desalination plants with other installations using high volumes of water (e.g. waste water treatment plants, electric power generation plants, etc.) to achieve dilution factors by blending options (e.g. Spain or California) [6].

Reuse and valorization of components of seawater desalination reverse osmosis (SWD-RO) brines in industrial applications can be beneficial both in terms of new hydric resources and environmental impact reduction of the brines disposal. Thus, this action fits appropriately in the framework of circular economy concept that is promoted for example by the EU commission [7]. However, some pre-treatments (such as separation, concentration, purification) are usually

necessary prior to the EDBM to ensure that concentrated brines are rich enough in NaCl and purified enough from divalent ions [8,9].

Electrodialysis (ED) has been identified as an efficient concentration step for SWD-RO brine to use as raw material in the chlor-alkali industry [10]. However, in this work ED with bipolar membranes (EDBM) has been proposed for the SWD-RO brine valorization as strong acids and bases. EDBM technology has successfully been applied for biochemical and food processing systems and is nowadays promoted for environmental applications (e.g. recovery or valorization of waste effluents for the production of acids and bases) [11–14]. Strong bases and acids are used in water desalination for adjusting the water quality in terms of organoleptic perception or pH adjustment or for uses as reagents for RO or UF membrane cleaning procedures [15]. Acid and base production from different effluents, such as sludge, wastewater with metals, diluate salt solutions or lake brines have also been studied recently [16–19]. Some studies dealing with seawater or brines to produce chemicals (acid and base) with EDBM at lab or pilot scale have been reported in literature [20–25]. Badruzzaman et al. [20] treated RO concentrate in an EDBM pilot plant with an active membrane area of 64 cm^2 and 0.2 M of mixed acid (HCl, HNO_3 and H_2SO_4) and base (NaOH, KOH) was acquired in 10 h of operation. Ibañez et al. [23] used synthetic RO brines as feed solution in an EDBM pilot plant of 200 cm^2 of membrane area and 1 M of acid (HCl) and base (NaOH) concentration was produced. Both mentioned studies concluded that the electrical consumption would be reduced with the increase of brine concentration.

Because scaling problems due to polyvalent species (calcium, magnesium) could appear if pH is not properly controlled [26], a pre-treatment of the brine is often required to reduce divalent cations concentration before the concentration step by EDBM. Nanofiltration (NF) has been used with highly concentrated brines in the chlor-alkali industry in order to remove sulfate [27,28], divalent cations [29] and also as a seawater pre-treatment [30] because of its ability to remove

polyvalent ions without significantly rejecting monovalent ions. Then, NF has been postulated by Telzhensky M. et al. and Lahav O. et al. as a brine pre-treatment step to produce rich Mg(II) and Ca(II) concentrates or $Mg(OH)_{2(s)}$ with potential interest for the recovery of phosphate from anaerobic digestion concentrates in wastewater treatment plants [31,32].

The aim of this work is (i) to remove and concentrate Mg(II) and Ca(II) by NF, producing a NaCl-rich brine with low Mg(II) and Ca(II) concentration, (ii) to purify the brine by chemical precipitation and (iii) to produce HCl and NaOH from the purified brine with EDBM in order to promote RO desalination in-plant acid-base production. The specific objectives are (i) to evaluate the selectivity and removal efficiency of NF under different inlet pressures, (ii) to optimize the pre-treatment precipitation process of divalent ions in order to use the NF permeate as feed solution in the EDBM, (iii) to optimize the operation conditions of the EDBM to maximize the final acid and base concentration and (iv) to estimate the specific energy consumption and current efficiency under such optimized conditions.

2. EXPERIMENTAL

Firstly, SWD-RO brines were used as feed solution for a NF system. Calcium and magnesium could be concentrated by means of NF, while producing a NaCl-rich brine. Then, a precipitation treatment was done to this stream in order to remove residual calcium and magnesium. Finally, the NaCl-rich brine was valorized by EDBM for acid-base production. A scheme of the process to be evaluated is represented in Figure 1.

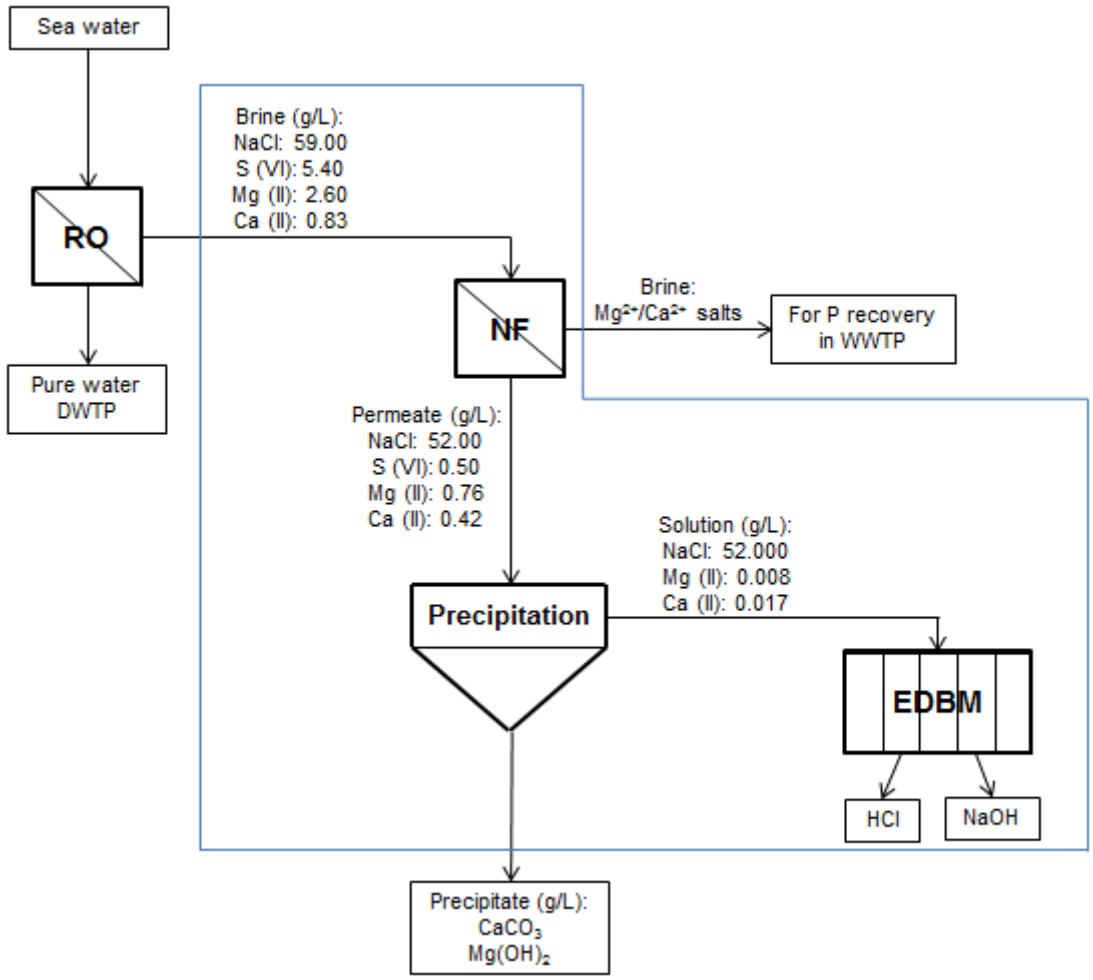

Figure 1. Schematic illustration of the seawater desalination brine valorization process. Stream concentrations are indicated on the arrows.

2.1. SWD-RO brine composition.

SWD-RO brine from the Desalination plant of Barcelona (NE, Spain) was used to carry out the experiments. Components in the SWD-RO brine can be distinguished as major and minor components depending on their concentrations. Concentration of major components are: 38.8 Cl(-I), 20.8 Na(I), 5.40 S(VI), 2.60 Mg(II), 0.83 Ca(II), 0.70 K(I) and 0.016 Sr(II) in g/L, whereas minor components concentrations are: < 1 SiO_2, 0.3 Al(III), <0.2 Fe(II,III), <0.2 Ba(II), 0.07 Ni(II), 0.03 Cu(II), 0.01Mn(II) and 0.007 Cr(III) in mg/L.

2.2. Removal of Ca(II)/Mg(II) from SWD-RO brines by NF

The pilot plant assembled five elements of NF270 4" 40" in series in a vessel providing a total active membrane of 38 m^2. All materials used in the construction of the pilot plant were especially chosen to resist corrosion of highly concentrated brine and also to resist high pressures in order to prevent membranes deterioration. NF270 membranes (Dow Chemical), composed of a semi aromatic piperazine-based polyamide layer on top of a polysulfone micro porous support reinforced with nonwoven polyester were chosen according to their high production flux and medium hardness removal capacity.

Antiscalants (1 mg/l) were added to the feed brine in order to avoid calcium and sulfate precipitation. After filtration through 5 microns filters, the inlet brine was pumped to the NF vessel at a flow rate of approximately 1250 L/h (33 L/m^2h). Different inlet pressures were evaluated in the range of 8 to 20 bars in order to assess the ion rejection and the final Ca(II) and Mg(II) concentrations. Samples of feed brine, permeate and reject brine were collected twice a day, for at least 3 days, when the system was stabilized after 48h of continuous operation. Flushing with permeate of the NF process or tab water was done after each experiment. Cleaning procedures with HCl or NaOH solutions to remove fouling were carried out when the salt removal efficiency was reduced by 10%, the nominal permeate flux diminished by 15% or when the difference between inlet and outlet pressure was higher than 15%.

Several parameters such as conductivity, pressure, flow rate and pH of each stream were monitored during the experiment (Figure 2a).

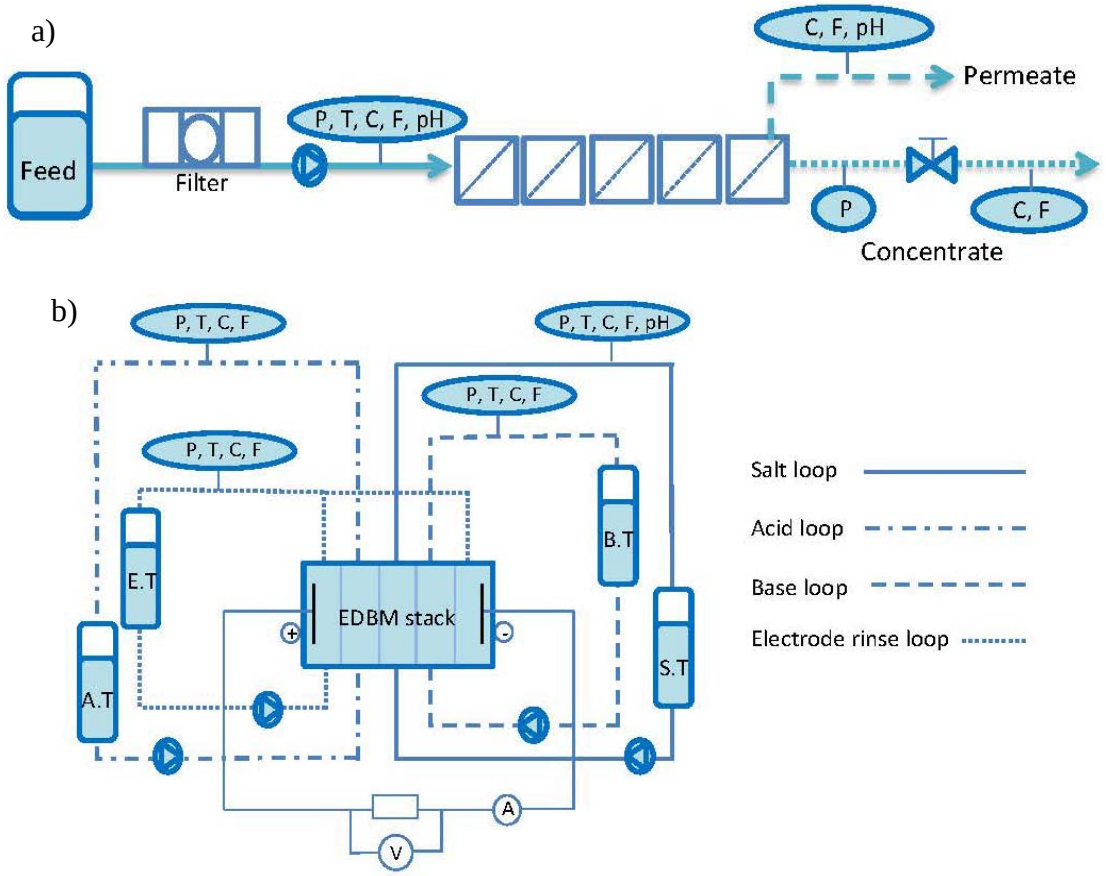

Figure 2. a) NF pilot plant scheme and b) EDBM pilot plant scheme. (P: pressure sensor, T: temperature sensor, C: conductivity sensor, F: flow-meter, pH: pH-meter, A: ammeter, V: voltmeter, S.T: salt tank, A.T: acid tank, B.T: base tank, E.T: electrode rinse tank).

2.3. Purification of NF permeate by precipitation

Because concentration of Ca(II) and Mg(II) were still high in the NF permeate (up to 415 mg/L for Ca(II) and up to 760 mg/L for Mg(II)) the EDBM module was prone to scaling by calcium and magnesium salts. A reduction of the Ca(II) and Mg(II) content prior to the EDBM unit was performed using mixtures of Na_2CO_3 and NaOH according to reactions (1-2):

$$Ca^{2+} + CO_3^{2-} \leftrightarrow CaCO_{3(s)} \quad (1)$$

$$Mg^{2+} + 2OH^- \leftrightarrow Mg(OH)_{2(s)} \quad (2)$$

Ca(II) and Mg(II) precipitation can be accelerated by increasing the temperature or by using an excess of Na_2CO_3 (from 0.3 and 1.5 g/L) and/or NaOH (from 0.1 to 0.5 g/L). Temperatures over 60ºC are recommended to speed up the purification process, which otherwise can take several hours to complete. Nevertheless, high brine temperatures can increase the precipitate settling rate as it reduces the crystal size [33,34].

After the precipitation process and before the EDBM filtration, pH was adjusted to values between 3-4 as recommended elsewhere [35].

2.4 Production of HCl and NaOH by EDBM

The EDBM stack used was a PCCell ED 64-004 (PCCell GmbH, Germany). It contained a 4 chamber system with an active membrane area of 0.0064 m^2 per membrane. Dimensions of the cell were 0.11 x 0.11 m. The stack configuration was composed of three cell triplets; each cell triplet had one cationic exchange membrane (CEM) (PC-SK), one anionic exchange membrane (AEM) (PC Acid 60) and one bipolar membrane (BM). The pilot plant worked by means of 4 recirculated circuits: the electrode rinse, acid, basic and diluate. Two electrodes rinse compartments formed a single circuit located at the cell ends. Moreover, each cell triplet had one acid, one basic and one dilute compartment.

NaCl solutions were prepared representing the permeate NF stream after the precipitation step in order to use them as raw solution of the EDBM process. Initial HCl and NaOH concentration were needed to avoid a high resistance in the power supply, thus HCl and NaOH solutions were prepared. Moreover, 45 gNa_2SO_4/L were used as electrode rinse salt solution in each experiment. All reagents used were of quality analysis (PA-ACS-ISO reagent, PANREAC). 1 L of each solution was prepared and recirculation configuration was used to carry out the experiments. Some experiments were performed at different constant voltage (9 and 6V) to evaluate the effect of this parameter on the final acid and base concentrations. Different initial

acid and base concentration (0.05, 0.1 and 0.5 M) were used to determine also their influence on the final concentration of HCl and NaOH.

The experiments were conducted in a batch-mode configuration and under constant voltage across the electrodes. 4 pumps boost each one of the streams into the EDBM stack. A power supply device (Manson, HCS-3202) was used to establish an electrical current density in the stack. The work pressure was 0.3 bars; acid, base and salt streams flow rate were ranged between 15 and 20 L/h, while the electrode rinse flow rate was approximately between 80 and 100 L/h. The maximum temperature allowed was 40 ºC.

Experiments were stopped when the conductivity in the feed stack was not high enough to keep constant the desired current density. Initial tests were carried out to select the most suitable operating conditions for the process, such as voltage applied or initial acid and base concentration.

During the experiments, potential and electrical current of the system, conductivity, flow rate, temperature, and pressure of each stream solution were recorded. Furthermore, pH of the diluted solution during the experiment was monitored by a pH-meter in the diluted circuit (Figure 2b).

2.5 Analytical methodologies and chemical analysis.

Samples from NF membrane experiments: Chloride concentration was determined potentiometrically through precipitation with $AgNO_3$ and using a silver chloride electrode in a METHROM 721 potentiometer. Calcium and magnesium concentrations were measured by atomic absorption spectrophotometry (AAS) using an Analyst 300 Perkin Elmer Spectrophotometer. Sulfate was determined by ionic chromatography (IC) using a 761 Compact IC Methrom equipped with an Anion Dual 2-6.1006.100 column. Potassium, strontium and trace metals (aluminum, copper, iron and nickel) were determined by inductively coupled plasma atomic emission spectroscopy (ICP-OES) using a Variant 725 ICP spectrophotometer.

Samples from EDBM membrane experiments: The conductivity of the salt, acid, base and electrode rinse streams was measured by means of conductivity sensors inside the pilot plant. HCl and NaOH concentrations were determined by acid-base titration (Titration Excellence T-70). Cation and anion concentration of each salt sample was measured by ionic chromatography (ICS-1000 and ICS-1100, respectively).

2.6 Data analysis

Determination of rejection using NF

Rejection (R) was calculated according to equation 3.

$$R = \left(1 - \frac{C_{permeate}}{C_{feed}}\right) \cdot 100 \quad (3)$$

Where $C_{permeate}$ and C_{feed} are permeate and feed concentrations, respectively.

Determination of energy consumption and current efficiency in the EDBM process

Energy consumption (Ec) and current efficiency (Ie) were calculated by means of equations 4 and 5, respectively.

$$Ec = \frac{(I \cdot U \cdot t)/1000}{\text{kg final product}} \quad (4)$$

Where I (A) and U (V) are the current and voltage applied in the EDBM stack, respectively, and t (h) is the time of the operation.

$$Ie = \frac{F \cdot (V_t \cdot C_t - V_i \cdot C_i)}{I_d \cdot S \cdot t \cdot n} \quad (5)$$

Where F is the faraday constant (96500 C/mol), V (L) and C (M) are the volume and concentration at time "t" or at initial time "i", I_d is the current density (A/cm^2), S the membrane surface (64 cm^2), t is the operational time (s) and n is the cell triplets of the EDBM stack (3 in this study).

3. RESULTS AND DISCUSSION

3.1 Removal of Ca(II)/Mg(II) from SWD-RO brines by NF

The NF pilot plant was operated using different inlet transmembrane pressures (TMP) from 8 to 20 bar. Rejection (R) data and composition of the SWD-RO brine and NF permeate stream obtained are compared as a function of transmembrane pressure in Table 1. The pH of the inlet brine was constant (≈7), for which permeability and retention properties have been reported optimum for NF270 membranes [36].

Table 1. Species rejection result (%) and permeate composition obtained with NF pilot plant using SWD-RO brine as a function of the transmembrane pressure.

Component	SWD-RO brine composition (mg/L)	NF permeate composition (mg/L)					% Rejection at 22-26ºC				
		8 bar	10 bar	12 bar	18 bar	20 bar	8 bar	10 bar	12 bar	18 bar	20 bar
NaCl	59000	57000	55000	54000	52000	52000	3±1.2	7±0.8	9±0.7	12±0.4	12±0.3
K (I)	700	670	666	670	670	664	4±0.6	5±0.4	4±0.2	4±0.3	5±0.2
Ca (II)	830	598	498	465	415	415	28±1.4	40±0.9	44±1.1	50±0.7	50±0.7
Mg (II)	2600	1200	1160	1000	920	760	54±0.8	55±0.7	62±0.5	70±0.7	71±0.4
S (VI)	5400	1200	1100	1100	600	500	78±1.8	79±1.5	79±1.2	89±1.1	91±0.9
Al (III)	0.3	<DL	<DL	<DL	<DL	<DL	>93	>93	>93	>93	>93
Ni (II)	0.07	0.069	0.069	0.063	0.054	0.045	0±5.2	0±7.1	10±5.6	23±5.7	35±5.4
Sr (II)	16	10.7	9.4	8.5	4.8	4.7	33±7.0	41±8.4	47±7.2	70±3.9	70±3.1
Cu (II)	0.03	0.025	0.023	0.020	0.010	0.010	17±6.3	23±4.6	33±5.5	67±4.7	67±5.6

Detection limit (DL): 0.0225 mg/L of aluminum

In the TMP range evaluated rejection of univalent ions (Na(I), Cl(I), K(I)) was lower than that of polyvalent ions (Ca(II), Mg(II), S(VI), Sr(II), Cu(II), Ni(II), Al(III)).

Rejection of polyvalent ions generally increased with pressure in the range studied (8 up to 20 bars), but undesired NaCl rejection also increased reaching a maximum of 12% at 20 bar. However, divalent ions were more rejected than NaCl, so the NF objective was achieved. Rejection of major ions became stable with the increase of pressure reaching a plateau at pressures of 18 bars with the exception of Ni (II). Rejection order with SWD-RO brine at 20 bar

was Al(III) > S (VI) > Mg (II) > Sr (II) > Cu (II) > Ca (II) > Ni (II) > NaCl > K (I). NF270 is a negatively charged membrane, so higher rejections were obtained with anions, in exception of the Al(III) which is a trivalent ion, and then it was more rejected by NF than divalent ions or monovalent ones [37,38].

Ionic size, shape, hydrated ion and initial concentration of an ion play a significant role in its rejection degree. As reported in the literature, when high concentrated brines are used, screen phenomenon strongly happens on membrane surface and Donnan effect of electric repulsion is minimized. Counter ions screen membrane surface charge and, in consequence, sieving becomes the significant mechanism for ion rejection [36] and ions with lower hydrated radius like Na(I) and K(I) are less rejected from the brine than the other ions [39]. It should be pointed out that at high concentration, formation of ion pairs may be significant and their radii are different from the radii of the free ions.

In Table 2, the speciation of ions with the fraction in which the specie is considered, hydrated radius, and rejections obtained at 20 bar are summarized. It can be observed that ions with higher hydrated radius tended to have higher rejection than those with lower hydrated radius. In conclusion, species size can be used as a first approach to predict the performance of NF, despite the complex mechanism of rejection that occurs on NF [37].

Table 2. Hydrated radius of ions studied, speciation and rejection obtained with SWD-RO brine at 20bar.

Element	Speciation of ions in the inlet brine*	Considered Form	Hydrated radius (nm)	Rejection at 20 bar
K(I)	K^+ (0.82) KCl_{aq} (0.18)	K^+	0.275	5%
Na(I)	Na^+ (0.98) $NaSO_4^-$(0.02)	Na^+	0.365	12%
Ca(II)	Ca^{2+} (0.45) $CaCl^+$ (0.35)	Ca^{2+}	0.349	50%

	$CaSO_{4(aq)}$ (0.20)			
Sr(II)	Sr^{2+} (0.65) $SrSO_{4aq}$ (0.30) $SrSO_{4(s)}$ (0.05)	Sr^{2+}	0.410	70%
Mg(II)	Mg^{2+} (0.65) $MgSO_{4\ aq}$(0.35)	Mg^{2+}	0.429	71%
Cl(-I)	Cl^{-}(1)	Cl^{-}	0.347	12%
S(VI)	$MgSO_{4aq}$ (0.70) $NaSO_4^-$ (0.18) SO_4^{2-} (0.04) $CaSO_{4aq}$ (0.08)	SO_4^{2-}	0.380	91%

*Brine speciation has been carried out by the PHREEQC numerical code and using the Pitzer data base [40].

The highest Mg(II)/Ca(II) concentrations in the concentrate stream were obtained at 20 bars, with values on the Ca(II) and Mg(II) concentration of 2.1 g/l and 8.3 g/l. Such Mg(II)-rich brine can be used in a cost effective fashion within a variety of water/waste water treatment processes as has been discussed by Telzhensky et al. [31]. For instance, Mg^{2+} can be added to post treated desalinated water in drinking water plants applications [41], while for waste water treatment applications it can be used for removal of inorganic phosphate species via precipitation of Mg-phosphates (struvite, $MgNH_4PO_4$) [32], Ca-phosphates (hydroxyapatite) [42], or Mg-Ca-phosphates (e.g. stanfieldite, farringtonite) [43], which are products potentially reusable as new phosphorous resources for fertilizers production or as for direct application to soils as slow release fertilizers [15]. Also the use of Mg(II)-rich brines for production of $MgSO_4$(s) by integration of a concentration step by membrane distillation and crystallization has been reported [44].

The highest rejections were observed at 20 bars with approximately 415 mg/L of calcium, 760 mg/L of magnesium, 500 mg/L of sulfate and 52 g/L of NaCl in the NF permeate stream (Table 1). These results are comparable with those reported by Madaeni et al. [29] and Hilal et al. [45]. Hilal et al. [45] treated synthetic solutions of 25 g/L NaCl with NF 270 membrane. It was concluded that at higher inlet concentrations, lower rejections were observed due to ion repulsions. It is

worth mentioning that rejections in the present study were in the range of the values reviewed by Hilal et al. when highly concentrated brines are used. On the other hand, Madaeni et al. [29] used different membranes to treat saturated chlor-alkali brine for calcium, magnesium, sulfate and iron removal. Optimal conditions were reported at 8 bar for PVD Hydranautics membranes. Lower permeate flow (9 L/m^{2}h) at the same pressure was observed for NF270 but rejections were similar in all ions analyzed (32% rejection of calcium and 40% of magnesium with a permeate flow of 16 L/m^{2}h). NF270 rejected more NaCl than most of the membranes reviewed.

3.2 Purification of NF permeate by precipitation

Concentrations of Ca(II) and Mg(II) in NF permeate stream (at 20 bars) were reduced up to 50 % and 71%, respectively as a first purification step, before the EDBM process.

However, a final polishing step through a precipitation treatment was needed in order to avoid scaling and precipitation during the acid and base production in the EDBM pilot plant.

The water quality characteristics of the SWD-RO NF permeate before and after precipitation treatment are collected in Table 3. Different pHs were studied depending on the Na_2CO_3 and NaOH dose added.

Table 3. Initial and final Ca(II) and Mg(II) concentrations before and after the precipitation treatment.

Precipitation	NF permeate concentration (mg/L)	pH	Removal (%)	Concentration after precipitation (mg/L)
Calcium with Na_2CO_3	415	8.6	0	415
		9.8	67±3	137.0
		10.2	93±3	29.1
		10.6	96±2	16.6
Magnesium with NaOH	760	9.1	0	760
		10.3	41±3	448.4

	10.6	76±4	182.4
	11.5	99±1	9.3

Higher removal was achieved at higher pH values. For example, $Mg(OH)_2$ precipitated when the pH value was higher than 10 [46]. Removal values of 96% for calcium (adding Na_2CO_3) and 99% for magnesium removal (with NaOH) were obtained. These removal percentages were higher than those reported in literature in a bioelectrochemical system [47]. In that case, 84% of Ca^{2+} and 37% of Mg^{2+} in seawater was effectively removed while treating wastewater in the anode chamber of the system.

Finally, the calcium and magnesium concentrations in the stream to be treated by EDBM were 16.6 mg Ca^{2+}/L and 9.3 mg Mg^{2+}/L (Figure 1) at higher pH values of 10.6 and 11.5, respectively. Those values were low enough to avoid scaling on the ion exchange membranes, due to selective membranes to monovalent ions were used for the EDBM process. Then, transport of the divalent ions towards the base stream was negligible.

3.3 Production of HCl and NaOH by EDBM

Figure 3 shows the conductivity evolution of each stream during experiments carried out with the EDBM pilot plant (acid, base, salt and electrode rinse) showing the desalinating of the NaCl brine while producing NaOH and HCl, as was previously reported by other authors [20,22]. Efficiency values, considering the NaCl percentage that was converted to HCl and NaOH, were higher than 70 %. As it was expected, the conductivity of the electrode rinse stream (Na_2SO_4) was constant along the whole experiment.

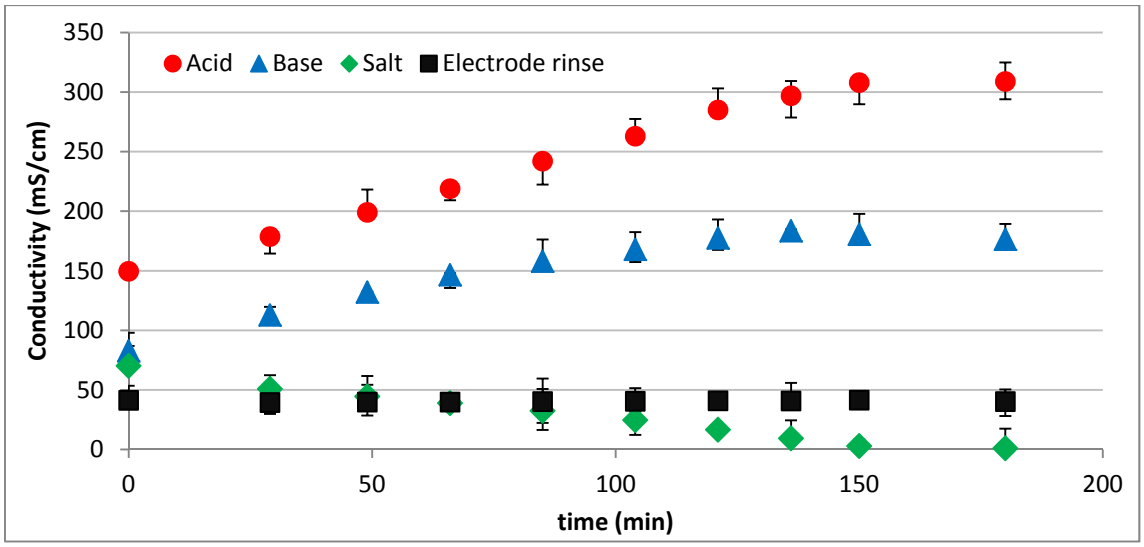

Figure 3. Conductivity evolution of the four stack stream during an EDMD experiment.

Voltage applied effect

The initial and final salt, acid and base concentrations working at different conditions of constant voltage (9V, ~0.5kA/m^2 and 6V, ~0.2kA/m^2), while keeping constant the initial HCl and NaOH concentration (0.10 M) and using the NF permeate concentration of approximately 50 g NaCl/L as feed salt solution are shown in Figure 4a.

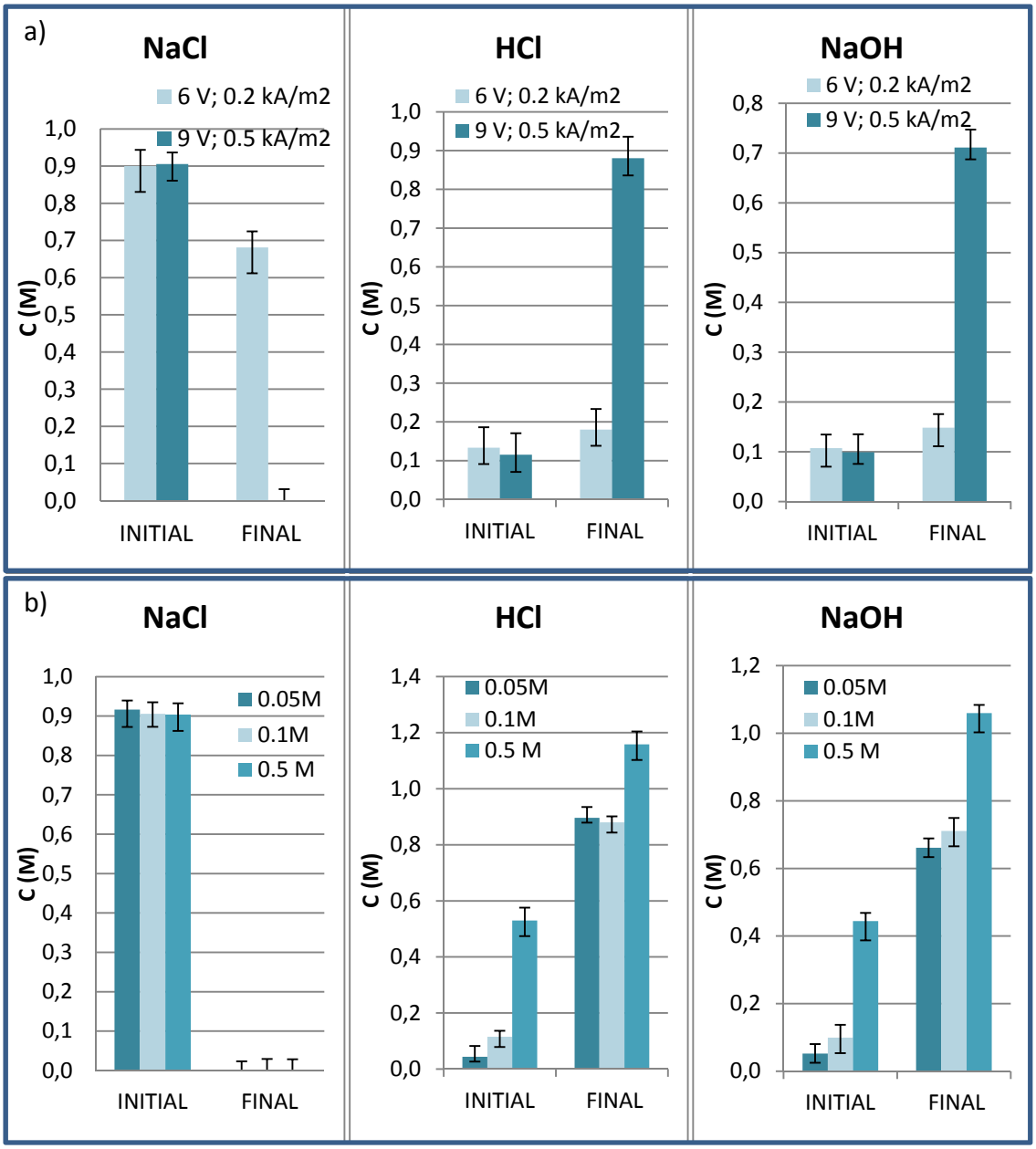

Figure 4. Salt, acid and base concentration at the initial and final experimental time under a) different current densities and maximum voltage and, b) different initial concentration of HCl and NaOH

Working at 6 V (~0.2 kA/m^2) it was possible to produce 0.18M HCl and 0.15M NaOH, while applying 9 V (~0.5 kA/m^2), the final concentration of HCl and NaOH were 0.88 and 0.71M, respectively. Low efficiency values, considering the NaCl percentage that was converted to HCl

and NaOH, of 20 % were obtained applying 6 V, while high conversion percentage of more than 70 % were achieved applying the high value of current density.

It can be stated that higher NaOH and HCl concentration were obtained at higher current density and voltage. This is in agreement with values reported in literature by other authors [20,21,23]. For instance, Badruzzaman et al. [20] studied the same EDBM process with an initial NaCl concentration of 87.75 g/L and concentrations achieved were HCl 0.15 M and NaOH 0.20 M working at 0.15 kA/m^2, while 0.75 and 0.55M were achieved for HCl and NaOH, respectively, applying a constant current density of 0.90 kA/m^2.

Experiments were then carried out at constant voltage of 9 V (~0.5kA/m^2) in order to increase the final acid and base concentration.

Initial acid and base concentration effect

To assess the initial acid and base concentration effect, different experiments were carried out changing their initial concentration (0.05, 0.1 and 0.5 M), but keeping constant the voltage applied (9 V) and also the initial NaCl concentration obtained from the NF experiments (approximately 50 g NaCl/L). The initial and final concentrations obtained are shown in Figure 4b.

Figure 4b shows that a total desalination of NaCl could be achieved up to the concentration values below the detection limit of the analysis equipment.

Conversion percentage values of NaCl into HCl and NaOH were higher than 70 %. Working with initial acid and base concentration of 0.1 M the conversion value was 93 %. Besides, concentrations of approximately 1 M of HCl and NaOH could be achieved. It seemed that few modifications (0.05 or 0.1 M) on the initial acid and base concentrations did not represent any substantial effect on the overall performance, although higher values of initial acid and base concentration (0.5 M) implied higher HCl and NaOH concentrations. In a previous study Tran et

al. [19] reported that the base produced remains unchanged when the initial concentration was higher than 0.2 M working at 0.4 kA/m^2.

Energy consumption and current efficiency

Nowadays, HCl is cheaper than NaOH, for this reason, the energy consumption (Ec) and current efficiency (I_e) were calculated as a function of NaOH concentration, and HCl was considered as a by-product. The initial and final concentrations of each stream, the quantity of HCl produced, the energy consumption to produce NaOH and the current efficiency working at 9 V (~ 0.5 kA/m^2) are summarized in Table 4.

Table 4. Experimental results of concentration and energy consumption

U	Ĩ	Electrode (Na_2SO_4)		Salt (NaCl)		Acid (HCl)		Base (NaOH)		Time	kg HCl	Ec (kWh/kg	Ie
(V)	(kA/m^2)	$C_{initial}$ (g/L)	C_{final} (g/L)	$C_{initial}$ (g/L)	C_{final} (g/L)	$C_{initial}$ (M)	C_{final} (M)	$C_{initial}$ (M)	C_{final} (M)	(h)	produced	NaOH produced)	(%)
8.98	0.41	45.50	43.59	53.60	0.01	0.06	0.90	0.05	0.66	2.44	0.031	2.345	85.6
8.91	0.44	44.66	43.85	52.98	0.01	0.12	0.88	0.10	0.71	2.54	0.028	2.576	77.3
8.91	0.47	46.86	45.03	52.88	0.02	0.53	1.16	0.44	1.06	2.68	0.023	2.888	68.9

The energy consumption values were around 2.6 kWh/kg NaOH working at a constant voltage of 9 V and using the SWD-RO NF permeate of 50 g NaCl/L. These value are in the same order of magnitude as the energy consumption reported by Ye et al. [14] of 3.07 kWh/kg NaOH, while Wei et al. [48] reported a higher value of 8.5 kWh/kg NaOH (working with a 2 compartments cell only for base production), working both at the same current density than this work (~ 0.5 kA/m^2).

According to these results it can be stated that at higher initial acid and base concentration, higher Ec was needed. On the other hand, less HCl was produced by increasing the initial acid concentration, so with little initial concentration values, such as 0.05 M HCl, approximately 1 M HCl can be obtained.

Moreover, the current efficiency for the valorization of SWD-RO brine as NaOH was around 77%. Different authors studied the current efficiency for similar systems and values between 65 and almost 100% were reported. Ye et al. [14] and Ibañez et al. [23] reported lower values than in the present study (I_e < 70 %), while Wei et al. [48] reported values almost of 100%, although working with 2 compartments cell only for base production, without simultaneous acid production.

Current efficiency decreased as initial NaOH concentration increased, due to more OH^- ions migrated from the base compartment to the salt compartment (because of the concentration gradient). This fact is comparable to the results previously reported by Tran et al. [19] and Ye et al. [14] where the higher current efficiency was achieved at lower initial NaOH concentration. A higher NaOH concentration implies a larger osmotic pressure in the system. Then, the water dissociation into protons and hydroxyl ions become more difficult due to less water is supplied into the bipolar membrane.

4. CONCLUSIONS

Aromatic polyamide NF membrane (NF270) provided a rich Mg(II) (8.3 g Mg(II)/L) and Ca(II) (2.1 g Ca(II)/L) concentrate stream from SWD-RO brine working at 20 bars with enrichment factors of 3.2 for Mg(II) and 2.5 for Ca(II). Rejection of polyvalent ions (Ca(II), Mg(II), S(VI), Sr(II), Cu(II), Ni(II), Al(III)) was higher than univalent ions (Na(I), Cl(I), K(I)), mainly dependent on the hydrated ionic radii and speciation. Rejection of undesired ions increased with pressure, undesired NaCl rejection also increased but maximum value of 12% was reached. Results are comparable with the results reported in literature for the use of nanofiltration for seawater pre-treatment. NaCl concentration slightly decreased after the NF treatment.

Results demonstrated that higher quality of brine was obtained when NF was used as a pre-treatment: with purities of 98% of NaCl which would benefit its subsequent reuse. Nevertheless, further a purification step for removal of Ca(II) and Mg(II) was needed to meet the EDBM

requirements. Removal values of more than 95% of calcium and magnesium were achieved using precipitation treatment by Na_2CO_3 (pH 10.6) and NaOH (pH 11.6) before EDBM process. Divalent cations free brines containing NaCl (50 gNaCl/L) were fed into the EDBM stack in order to produce NaOH and HCl under recirculation configuration. According to the results, EDBM is a suitable method for desalinating brines producing acid and base, in this study HCl and NaOH were produced from NaCl. Conversion percentage of HCl and NaOH from NaCl were higher than 70 %. It was found that an increase of the applied voltage represented higher NaOH and HCl concentration. Furthermore, initial acid and base concentrations represented no substantial effect on the overall performance. For energy consumption and current efficiency, values around 2.6 kWh/kg NaOH and 77%, respectively, were obtained.

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